

**FRACTURE TOUGHNESS ENHANCEMENT OF ZIRCONIA TOUGHENED
ALUMINA (ZTA) THROUGH ADDITIONS OF COMBINATION OF CaCO_3
AND CaO**

by

ZHWAN DILSHAD IBRAHM SKTANI

Thesis submitted in fulfilment of the requirements

for the degree of

Doctor of Philosophy

September 2016

AUTHOR'S DECLARATION

I hereby declare that I have conducted, completed the research work and written the dissertation entitled "FRACTURE TOUGHNESS ENHANCEMENT OF ZIRCONIA TOUGHENED ALUMINA (ZTA) THROUGH ADDITIONS OF COMBINATION OF CaCO_3 AND CaO ". I also declare that it has not been previously submitted for the award of any degree or diploma or other similar title of this or any other examining body or university.

Signature of candidate:

Name of candidate: Zhwan Dilshad Ibrahim Sktani

Date:

Witness by:

Signature of witness (main supervisor):

Name: Professor Hj. Zainal Arifin b. Hj. Ahmad

Date:

ACKNOWLEDGEMENT

In the name of God the most gracious the most merciful.

Praise to Allah, the Cherisher and Sustainer of the worlds, for making this thesis a reality.

I have ever thought that to have someone to thank is a great luck. Every “thanks” comes from a relationship, an exchange, an enrichment. Each of these links is like a thread made of a different material, one is made of steel, another one is made of silk, others are extensible like elastomers, some of these are like glass fibers and we know how different are the properties of these materials! Some of these threads will break, others, I hope, will last long, and new ones will be woven. During the last years, these threads have created a particular structure, thanks to the several properties offered by the different materials. This structure has been strong and tough, able to absorb vibrations in a specific frequency range and to give some impulses at the right moment. Sometimes I have stumbled on any thread, because of my awkward character. Change is hard! But this structure gave me support, and it is almost superfluous to say that without this complex and amazing construction, perhaps this PhD thesis would not have been written

I am extremely grateful to Professor Dr. Hj. Zainal Arifin Hj. Ahmad for providing me the opportunity to work on this challenging project. This thesis would have not been possible without his valuable supervision, great patience and friendly encouragement. His inspiration, motivation and professionally guiding me were key points to successfully complete my research work. I would like to also thank him for providing me with outstanding research facilities and numerous technical discussions which I found to be very valuable to my research. His constant enthusiasm and

insightfulness will be a model for my career. Words are not enough to express my special thankful to him. His kind and continuous help will never be forgotten. I would like to express my great appreciation to Professor Dr. Mani Maran a/l Ratnam for his contribution on the cosupervision and valuable suggestions for this research and thesis.

Next, I would like to convey my special thanks to dean, Professor Dr. Zuhailawati binti Hussain, Deputy Deans, lecturers and all staffs of the School of Materials and Mineral Resources Engineering, Universiti Sains Malaysia (USM), for their kind assistant and supports. Without their kind cooperation, this study may not be completed on time.

My gratitude to Mr. Khairi, Mr. Mokhtar, Mr. Farid, Mr. Zaini, Mr. Shafik and Mr. Sharul for their experimental and technical assistant. I am also thankful to friends and colleagues; Dr. Azhar, Dr. Dr. Nik, Dr. Fahmin, Dr. Rashid and Dr. Ali Arab for their support, valuable advises and kind support.

Finally, my deepest thankful for my parents. Their constant support, encouragement gives me warmth and strength to me. They always are there to share my success as well during sad and down times. Their inspiration, understanding, patience and support help me to complete this thesis and no words are sufficient to express my appreciation to both of them.

TABLE OF CONTENTS

| | |
|----------------------------|-------|
| Acknowledgement..... | ii |
| Table of Contents | iv |
| List of Tables | ix |
| List of Figures | x |
| List of Abbreviations..... | xvi |
| List of Symbols..... | xviii |
| Abstrak | xxi |
| Abstract | xix |

CHAPTER 1 - INTRODUCTION

| | |
|-------------------------------|---|
| 1.1 Research background | 1 |
| 1.2 Problem Statement | 4 |
| 1.3 Research Objectives | 6 |
| 1.4 Project Approach | 6 |

CHAPTER 2 - LITERATURE REVIEW

| | |
|---|----|
| 2.1. Zirconia Toughened Alumina (ZTA) | 9 |
| 2.2. Toughening mechanisms of ZTA | 10 |
| 2.2.1. Microcrack Toughening | 12 |
| 2.2.2. Stress Induced Transformation Toughening | 13 |
| 2.2.3. Compressive Surface Stress | 14 |
| 2.3. Toughness Enhancement of ZTA | 15 |
| 2.4. Contribution of Elongated Grains on Fracture Toughness Improvement | 17 |

| | |
|---|----|
| 2.4.1. Crack Deflection Mechanism | 18 |
| 2.4.2. Crack bridging Mechanism | 19 |
| 2.5. Fracture Modes | 20 |
| 2.6. Hexaluminates | 22 |
| 2.7. Hibonite in The CaO-Al ₂ O ₃ System | 25 |
| 2.8. Hobonite (CaAl ₁₂ O ₁₉) as Toughness enhancer of ZTA | 28 |
| 2.9. Fabrication Method | 30 |
| 2.10. Sintering Techniques | 33 |
| 2.10.1. Conventional Sintering | 34 |
| 2.10.2. SPS | 35 |
| 2.10.3. HIP | 36 |
| 2.10.4. SLS | 37 |
| 2.11. Sintering temperature | 38 |
| 2.11.1. Effect of Sintering temperature and soaking time on the CaAl ₁₂ O ₁₉ Formation | 39 |
| 2.12. Design of Experiment | 40 |
| 2.12.1. Surface Response Methodoogy (RSM) | 42 |
| 2.12.1. (a) Central Composite Design (CCD) | 44 |
| 2.12.2. Related Analysis in DOE | 46 |
| 2.12.2. (a) Analysis Of Variance (ANOVA) | 46 |
| 2.12.2. (b) Lack of Fit (LOF) | 47 |
| 2.12.2. (c) Residual Analysis | 47 |
| 2.12.2. (d) 3D Plot | 48 |
| 2.12.3. Software | 49 |

| | |
|---------------------|----|
| 2.13. Summary | 50 |
|---------------------|----|

CHATER 3 - METHODOLOGY

| | |
|---|----|
| 3.1. Experimental Design | 51 |
| 3.2. Raw Materials | 54 |
| 3.3. First Part: Determination Effect of CaCO_3 Addition on ZTA Toughness Improvement | 54 |
| 3.3.1. Preparation of Pellets | 54 |
| 3.4. Second Part: Determination Effect of the Addition of Combination of CaO and CaCO_3 on ZTA Mechanical Properties Enhancement | 56 |
| 3.4.1. Preparation of Pellets | 56 |
| 3.5. Third Part: Determination the Combined Effect of Sintering Temperature, Soaking Time and Combination Addition of CaO and CaCO_3 on the Fracture Toghness Improvement of ZTA | 57 |
| 3.5.1. Preparation of Pellets | 57 |
| 3.6. Characterisation | 58 |
| 3.6.1. Phase Identification and Quantitative Analysis | 58 |
| 3.6.2. Microstructure Observation | 59 |
| 3.6.3. Physical properties | 59 |
| 3.6.4. Mechanical Tests | 60 |
| 3.7. Design of Experiment and Analysis | 62 |

CHAPTER 4 - RESULTS AND DISCUSSION

| | |
|-------------------------|----|
| 4.1. Introduction | 64 |
|-------------------------|----|

| | | |
|--------|--|-----|
| 4.2. | Characterisation of the Raw Materials | 64 |
| 4.2.1. | Al ₂ O ₃ | 64 |
| 4.2.2. | YSZ | 66 |
| 4.2.3. | CaCO ₃ | 68 |
| 4.2.4. | CaO | 69 |
| 4.3. | Effect of CaCO ₃ on the Fracture Toughness Enhancement of ZTA | 70 |
| 4.3.1. | Phase Identification and Quantitative Data | 70 |
| 4.3.2. | Microstructure Observation | 73 |
| 4.3.3. | Physical Properties | 76 |
| 4.3.4. | Fracture Toughness | 77 |
| 4.3.5. | Hardness | 82 |
| 4.3.6. | Summary..... | 84 |
| 4.4. | Effect of CaO Addition on the Mechanical Properties Improvement of ZTA Added with CaCO ₃ | 84 |
| 4.4.1. | Phase Identification and Quantitative Data | 84 |
| 4.4.2. | Microstructure Observation | 87 |
| 4.4.3. | Physical Properties | 91 |
| 4.4.4. | Hardness | 92 |
| 4.4.5. | Fracture Toughness | 95 |
| 4.4.6. | Summary | 102 |
| 4.5. | Enhancement of Fracture Toughness Through Optimisation of Combinations CaO and CaCO ₃ Additions, Sintering Temperature and Soaking Time | 102 |
| 4.5.1. | Effect of Sintering Temperature on the Mechanical properties of ZTA..... | 103 |
| 4.5.2. | Effect of soaking time on the Mechanical properties of ZTA | 108 |

| | |
|---|-----|
| 4.5.3. Optimisation Process | 111 |
| 4.5.3. (a) Conformation of Vickers Hardness and Fracture Toughness by ANOVA | 112 |
| 4.5.3. (b) Influence of Process Parameters on Fracture Toughness and Vickers Hardness | 115 |
| 4.5.3. (c) Optimisation Process Using RSM | 118 |
| 4.5.3. (d) Confirmation Experiments | 119 |
| 4.5.3. (e) Residual Analysis | 120 |
| 4.6. Summary | 121 |

CHAPTER 5 - CONCLUSIONS AND FUTURE RECOMMENDATIONS

| | |
|-----------------------------------|-----|
| 5.1. Conclusions | 123 |
| 5.2. Future Recommendations | 125 |
| References | 126 |

List of Publications

LIST OF TABLES

| | Page |
|---|------|
| Table 2.1 Theoretical compositions and physical properties of CaO, Al ₂ O ₃ and different calcium aluminates (C= CaO and A = Al ₂ O ₃). | 27 |
| Table 2.2 General guide to evaluate values of R ² | 46 |
| Table 3.1 Raw materials used in the current study | 54 |
| Table 3.2 Amount of raw powders used for ZTA added with CaCO ₃ | 55 |
| Table 3.3 Amount of raw powders used for ZTA added with CaO & CaCO ₃ | 56 |
| Table 3.4 Amount of raw powders used for optimised ZTA added with CaO and CaCO ₃ | 58 |
| Table 3.5 Process Design layout using FCC | 63 |
| Table 4.1 Quantitative results of YSZ powder | 67 |
| Table 4.2 Quantitative results of sintered samples | 72 |
| Table 4.3 Quantitative results for sintered ZTA samples, added with CaO wt. % | 86 |
| Table 4.4 Average aspect ratio of CaAl ₁₂ O ₁₉ grains | 89 |
| Table 4.5 Process Design layout using FCC and test results | 111 |
| Table 4.6 ANOVA for response surface quadratic model hardness | 113 |
| Table 4.7 ANOVA for response surface quadratic model fracture toughness | 114 |
| Table 4.8 The optimised values for responses and highest value of desirability | 119 |

LIST OF FIGURES

| | | Page |
|-------------|--|------|
| Figure 1.1 | Figure 1.1: Overview of Research | 8 |
| Figure 2.1 | Phase transformation of ZrO_2 with temperature | 11 |
| Figure 2.2 | Microcrack toughening mechanism | 12 |
| Figure 2.3 | Schematic illustration of stress-induced phase transformation toughening | 14 |
| Figure 2.4 | Diagram of a section through a free surface at (a) the sintering temperature. On cooling, particles of ZrO_2 near the surface (b) transform due to reduced constraint, developing a compressive stress in the matrix. The thickness of this compressively stressed layer can be increased. (c) by abrasion of machining. | 15 |
| Figure 2.5 | crack bridging (labeled as '1'), crack deflection (labeled as '2') and crack cutting through a $CaAl_{12}O_{19}$ grain (labeled as '3') | 20 |
| Figure 2.6 | Crack path A: intergranular fracture, B: transgranular fracture and C: transgranular fracture with crack deviation | 21 |
| Figure 2.7 | β -Alumina and magnetoplumbite structures. Mirror planes viewed along the c-axes are given below each structure | 23 |
| Figure 2.8 | Phase diagram of $CaO-Al_2O_3$ system | 25 |
| Figure 2.9 | Images of conventional furnaces. (a) is box furnace and (b) is tube furnace | 35 |
| Figure 2.10 | A schematic illustration of SPS (a) and an image of SPS (b) | 36 |
| Figure 2.11 | A schematic illustration of HIP (a) and an image of HIP (b) | 37 |

| | | |
|-------------|--|----|
| Figure 2.12 | A schematic illustration of SLS process | 37 |
| Figure 2.13 | Stages of sintering (a) free particles, (b) necking between particles, (c) formation of grain boundary, and (d) densification process and pores elimination | 39 |
| Figure 2.14 | Experimental planning using DOE | 41 |
| Figure 2.15 | The normal probability plot | 48 |
| Figure 2.16 | 3D surface plot as a function of two factors, (a) maximum response, (b) no exact maximum or minimum response, and (c) plateau response, respectively | 49 |
| Figure 3.1 | Flowchart of first part. (Effect of CaCO_3 addition on the mechanical properties of ZTA at 1600 °C and 4 hr) | 52 |
| Figure 3.2 | Flowchart of second part. (Effect of CaO and CaCO_3 additions on the mechanical properties of ZTA at 1600 °C and 4 hr) | 53 |
| Figure 3.3 | Flowchart of the third part. (Optimisation of interaction effects of sintering temperature, soaking time and combination between CaO and CaCO_3 additions on the toughness improvement of ZTA ceramics) | 53 |
| Figure 3.4 | Sintering profile for ZTA samples added with CaCO_3 | 55 |
| Figure 3.5 | Sintering profile for ZTA samples added with CaO & CaCO_3 | 57 |
| Figure 3.6 | Schematic view for a crack due to the Vickers hardness indentation test | 61 |
| Figure 4.1 | XRD for Al_2O_3 powder. A, represents Al_2O_3 | 65 |
| Figure 4.2 | Morphology of Al_2O_3 particles at 5K magnification | 65 |

| | | |
|-------------|---|----|
| Figure 4.3 | XRD analysis for YSZ powder. m represents Baddeleyite and t represents tetragonal ZrO_2 | 66 |
| Figure 4.4 | Morphology of YSZ particles at 5K magnification | 67 |
| Figure 4.5 | XRD analysis for CaCO_3 powder. Ca, represents CaCO_3 | 68 |
| Figure 4.6 | Morphology of CaCO_3 particles at 5K magnification | 68 |
| Figure 4.7 | XRD pattern of CaO powders. CO represents CaO and C represents Ca(OH)_2 | 69 |
| Figure 4.8 | Morphology of CaO particles at 5K magnification | 70 |
| Figure 4.9 | X-ray diffraction diagrams of ZTA samples added with different CaCO_3 wt. % | 71 |
| Figure 4.10 | FESEM micrographs of surfaces of ZTA, added with A: 0.0% CaCO_3 , B: 0.5% CaCO_3 , C: 2.0% CaCO_3 , D: 5.0% CaCO_3 and E: 13.0% CaCO_3 | 74 |
| Figure 4.11 | : EDX analysis for ZTA added with 2.0% CaCO_3 (A) ZrO_2 , (B) Al_2O_3 and (C) $\text{CaAl}_{12}\text{O}_{19}$ | 75 |
| Figure 4.12 | Bulk density and percentage of porosity for ZTA samples as a function of CaCO_3 wt. %. | 77 |
| Figure 4.13 | Fracture toughness of ZTA samples as a function of CaCO_3 wt. %. | 78 |
| Figure 4.14 | Micrograph of crack propagation after indentation for pure ZTA | 78 |
| Figure 4.15 | Micrograph of crack propagation after indentation for ZTA added with CaCO_3 0.5 wt. % | 79 |

| | | |
|-------------|---|----|
| Figure 4.16 | Micrograph of crack propagation after indentation for ZTA added with CaCO_3 2.0 wt. % | 80 |
| Figure 4.17 | Micrograph of crack propagation after indentation for ZTA added with CaCO_3 5.0 wt. % | 81 |
| Figure 4.18 | Micrograph of crack propagation after indentation for ZTA added with CaCO_3 13.0 wt. % | 82 |
| Figure 4.19 | : Vickers hardness of ZTA– CaCO_3 samples as a function of CaCO_3 wt. %. | 83 |
| Figure 4.20 | X-ray diffraction diagrams of ZTA samples, added with different CaO wt. % | 85 |
| Figure 4.21 | FESEM micrographs for ZTA surfaces samples added with CaO wt. % (A) 0.0, (B) 0.1, (C) 0.2, (D) 0.3, (E) 0.4 and (F) 0.5 | 87 |
| Figure 4.22 | EDX analysis for the ZTA sample added with 0.2 wt. % CaO. (a) Al_2O_3 , (b) YSZ and (c) $\text{CaAl}_{12}\text{O}_{19}$ | 88 |
| Figure 4.23 | FESEM micrographs for ZTA surfaces samples added (A) with 0.5 wt. % CaCO_3 and (B) with 0.5 wt. % CaO | 90 |
| Figure 4.24 | Bulk Density and porosity of percentage of ZTA samples as a function of CaO increase (wt%). | 92 |
| Figure 4.25 | Vickers hardness of the ZTA samples as a function of CaO increase (wt. %) | 93 |
| Figure 4.26 | The fracture toughness of the ZTA samples as a function of CaO increase (wt. %) | 96 |

| | | |
|-------------|--|-----|
| Figure 4.27 | Micrograph of Crack propagation after indentation for ZTA added with 0.0 wt.% CaO | 96 |
| Figure 4.28 | Micrograph of Crack propagation after indentation for ZTA added with 0.1 wt.% CaO | 97 |
| Figure 4.29 | Micrograph of Crack propagation after indentation for ZTA added with 0.2 wt.% CaO | 98 |
| Figure 4.30 | Micrograph of Crack propagation after indentation for ZTA added with 0.3 wt.% CaO | 99 |
| Figure 4.31 | Micrograph of Crack propagation after indentation for ZTA added with 0.4 wt.% CaO | 100 |
| Figure 4.32 | Micrograph of Crack propagation after indentation for ZTA added with 0.5 wt.% CaO | 101 |
| Figure 4.33 | XRD diagrams for ZTA Samples at different sintering temperatures | 104 |
| Figure 4.34 | FESEM micrographs for ZTA 2 wt.% (CaO+CaCO ₃) at 1400 °C, 1500 °C and 1600 °C | 105 |
| Figure 4.35 | Bulk Density and percentage Porosity for ZTA (2.0 wt.% added with CaO+CaCO ₃) as a function of sintering temperature | 106 |
| Figure 4.36 | : Micrograph of crack propagation of ZTA (2.0 wt. % added with CaO and CaCO ₃) at different sintering temperatures | 108 |
| Figure 4.37 | XRD diagrams for ZTA (2.0 wt. % of CaO and CaCO ₃ addition) 1400 °C at different soaking times | 109 |

| | | |
|-------------|--|-----|
| Figure 4.38 | FESEM backscattered images for ZTA 2.0 wt. % added with CaO and CaCO ₃ at 1400 °C | 110 |
| Figure 4.39 | Interaction effect of sintering temperature and combination addition of CaO and CaCO ₃ on the fracture toughness of ZTA | 115 |
| Figure 4.40 | Interaction effect of sintering temperature and combination addition of CaO and CaCO ₃ on the hardness of ZTA | 116 |
| Figure 4.41 | Interaction effect of soaking time and combination addition of CaO and CaCO ₃ on the fracture toughness of ZTA | 117 |
| Figure 4.42 | Interaction effects of soaking time and combination addition of CaO and CaCO ₃ on the hardness of ZTA | 118 |
| Figure 4.43 | predict response vs actual response of hardness | 120 |
| Figure 4.44 | predict response vs actual response of fracture toughness | 121 |

LIST OF ABBREVIATIONS

| | |
|---------------|---|
| ANOVA | Analysis of Variance |
| ASTM | American Standard for Testing Materials |
| BBD | Box-Behnken Design |
| CA | CaAl_2O_4 |
| CA_2 | CaAl_4O_7 |
| CA_6 | $\text{CaAl}_{12}\text{O}_{19}$ |
| CCD | Central Composite Design |
| CTE | Coefficients of Thermal Expansion |
| DF | Degree of Freedom |
| DM | Dolehert Matrix |
| DOE | Design of Experiment |
| EDX | Energy Dispersive X-ray |
| F-test | Fisher test |
| FCC | Face Centred Cube |
| FESEM | Field Emission Scanning Electron Microscope |
| FT | Fracture Toughness Model |
| GFD | General Factorial Design |
| GOF | Goodness of Fit |
| GPa | Giga Pascal |
| HIP | Hot Isostatic Pressing |
| HV | Vickers hardness |
| kgf | Kilogram-force |

| | |
|--------------------|---|
| ICDD | International Centre for Diffraction Data |
| ISO | International Standard Organization |
| LOF | Lack of Fit |
| MLR | Multiple Linear Regression |
| MOR | Modulus of Rupture |
| MPa | Mega Pascal |
| MR | Multiple regression |
| m-ZrO ₂ | Monoclinic Zirconia |
| RSM | Response Surface Methodology |
| SEM | Scanning Microscope Electron |
| t-ZrO ₂ | Tetragonal Zirconia |
| wt. % | Weight percentage |
| XRD | X-ray diffraction |
| YSZ | Yttria Stabilised Zirconia |
| ZTA | Zirconia Toughened Alumina |

LIST OF SYMBOLS

| | |
|-----------------|---|
| A | Calcination Temperature |
| a | Half Of The Indentation Diagonal Length |
| B | Particle Size |
| b _o | Coefficient Of Intercept |
| b _i | Coefficient Of Intercept |
| b _{ii} | Coefficient Of Intercept |
| b _j | Coefficient Of Intercept |
| C | Concentration of Reactants |
| E | Modulus Young |
| HV | Vickers hardness |
| K _{Ic} | Fracture toughness |
| k | Number Of Factors |
| l | Length of the radiant crack |
| N | Number of Experiments |
| n | Number of Centre Points |
| (t) | Tetragonal phase |
| (m) | Monoclinic phase |
| X _i | Independent Variable |
| X _j | Independent variable |
| Y | Response |
| α | Rotatability |
| β | Error Function |
| ρ_b | Bulk density |

PENINGKATAN KELIATAN PATAH ALUMINA DIPERKUAT ZIRKONIA (ZTA) MELALUI PENAMBAHAN GABUNGAN CaCO_3 DAN CaO

ABSTRAK

Alumina yang diperkuat zirkonia (ZTA) merupakan sebatian seramik yang amat berguna dalam teknologi industri masa kini. Walau bagaimanapun, sifat keliatan patah ZTA yang rendah menghadkan penggunaan yang meluas dalam bidang kejuruteraan. Oleh itu, penambahbaikan bagi keliatan patah adalah penting. Oleh yang demikian, kepentingan untuk mengekalkan kekerasan yang tinggi dan meningkatkan keliatan patah akan meningkatkan kebolehpercayaan penggunaan ZTA dalam aplikasi teknologi. Pembentukan *in situ* butiran memanjang CaAl_2O_9 di dalam seramik ZTA ketika proses pensinteran menjadi pilihan. Keadaan ini disebabkan ia lebih mudah disinter, selamat dari bahaya kesihatan dan untuk mengelakkan kaedah pensinteran yang rumit dan kurang ekonomik. Serbuk-serbuk CaO dan CaCO_3 telah ditambah ke dalam ZTA, diadun basah, dimampat ekapaksi dan pembentukan ZTA melalui pensinteraan keadaan pepejal tanpa dikenakan tekanan. Kajian ini dibahagikan kepada tiga bahagian. Bahagian pertama ialah penambahan hanya CaCO_3 ke dalam ZTA. Keliatan patah meningkat dari $5.95 \text{ MPa.m}^{1/2}$ untuk ZTA tulen kepada $6.3 \text{ MPa.m}^{1/2}$ untuk ZTA ditambah dengan 0.5 wt.% CaCO_3 disebabkan oleh mekanisme pesongan retak di sepanjang butiran CaAl_2O_9 . Walau bagaimanapun, nilai kekerasan menurun disebabkan oleh penguraian CaCO_3 yang membebaskan CO_2 dan membentuk mikrostruktur berliang. Oleh itu, melalui penambahan gabungan CaO dan CaCO_3 ke dalam ZTA untuk mengurangkan keliangan dan serentak dengan itu mendapatkan butir-butir memanjang CaAl_2O_9 yang meningkatkan keliatan patah ZTA melalui mekanisme-mekanisme pesongan retak dan

penyambungan retak. Di dalam bahagian kedua, gabungan penambahan di antara CaO dan CaCO_3 telah ditetapkan pada 0.5 wt.%. Kekerasannya telah meningkat dan menghasilkan keliatan patah yang lebih baik disebabkan mikrostuktur ZTA yang kurang berliang dan saiz serta bentuk butir-butir CaAl_2O_9 yang terkawal. Komposisi optimum ZTA ialah dengan gabungan penambahan 0.4 wt.% CaO dan 0.1 wt.% CaCO_3 . Komposisi ini memberikan keliatan patah maksimum ($6.51 \text{ MPa.m}^{1/2}$) dan kekerasan yang berpatutan (1592 HV). Oleh itu, nisbah 4:1 untuk CaO: CaCO_3 telah dipilih sebagai asas kepada bahagian ketiga eksperimen. Bahagian ketiga ialah kajian mengenai kesan-kesan interaksi bagi tiga parameter, suhu pensinteran, tempoh rendaman dan gabungan di antara CaO dan CaCO_3 ke atas pengukuhan keliatan patah dan kekerasan Vickers ZTA. Rekabentuk Eksperimen (DOE) telah dilakukan untuk mengurangkan bilangan ujian dan sementara itu, proses pengoptimuman dijalankan untuk mengoptimumkan julat berkesan setiap respon. Selepas menggunakan Metodologi Permukaan Respon (RSM), adalah dibuktikan bahawa tempoh suhu pensinteran ialah pembolehubah yang paling berpengaruh terhadap keliatan patah dan kekerasan seramik ZTA. Keputusan optimum (keliatan patah ialah $6.84 \text{ MPa.m}^{1/2}$ dan kekerasan 1615 HV) diperolehi dari suhu pensinteran pada 1600°C , gabungan di antara CaO dan CaCO_3 0.95 wt.% dan tempoh rendaman 2.14 jam. Rekabentuk-rekabentuk lain seperti Analisis Varians (ANOVA), kekurangan penyesuaian, pemetaan 3D dan Analisis Baki telah mengesahkan kesesuaian keputusan yang diperolehi. Walau bagaimanapun, pengesahan keputusan yang diperolehi daripada eksperimen-eksperimen menunjukkan bahawa keputusan optimum (keliatan patah ialah $7.1 \text{ MPa.m}^{1/2}$ dan kekerasan 1584 HV) yang diperolehi daripada 1.05 wt.% gabungan di antara CaO dan CaCO_3 , suhu pensinteran pada 1600°C , dan tempoh rendaman 2.9 jam. Nilai-nilai ini adalah standing dengan formula daripada RSM.

FRACTURE TOUGHNESS ENHANCEMENT OF ZIRCONIA TOUGHENED ALUMINA (ZTA) THROUGH ADDITIONS OF COMBINATION OF CaCO_3 AND CaO

ABSTRACT

Zirconia Toughened Alumina (ZTA) is a successful ceramic compound in new technological industry. However, its low fracture toughness limited the usage of ZTA in many engineering applications. Therefore, the enhancement of fracture toughness is necessary. Nonetheless, it is crucial to maintain high hardness and enhance the fracture toughness to make ZTA more reliable for technological applications. In-situ formation of elongated $\text{CaAl}_{12}\text{O}_{19}$ grains inside ZTA ceramics during sintering process is preferred. This is due to its easy to be sintered, safety from health hazards and to avoid more complicated and less economical methods of sintering. CaO and CaCO_3 powders were added into ZTA, wet-mixed, uniaxially pressed and ZTA samples formed by pressureless solid state sintering. The current study is divided to three parts. The first part is the addition of CaCO_3 alone into ZTA. The fracture toughness was improved from $5.95 \text{ MPa.m}^{1/2}$ for pure ZTA to $6.3 \text{ MPa.m}^{1/2}$ for ZTA added with 0.5 wt. % of CaCO_3 due to crack deflection mechanism along elongated $\text{CaAl}_{12}\text{O}_{19}$ grains. However, the hardness decreased due to emission of CO_2 which creates porous microstructure. Hence, CaO and CaCO_3 added together into ZTA to reduce the porosity and simultaneously, obtain elongated $\text{CaAl}_{12}\text{O}_{19}$ grains which enhances the fracture toughness of ZTA through crack deflection and crack bridging mechanisms. In the second part, combination addition between CaO with CaCO_3 was fixed at 0.5 wt. %. The hardness was improved and better fracture toughness was obtained due to less

porous microstructure of ZTA and control of the size and shape of $\text{CaAl}_{12}\text{O}_{19}$ grains. The optimum ZTA composition was added with 0.4 wt. % CaO combined with 0.1 wt. % CaCO_3 . This composition has the maximum fracture toughness ($6.51 \text{ MPa.m}^{1/2}$) and reasonable hardness (1592 HV). Therefore, the CaO/ CaCO_3 ratio of 4:1 was selected as the base for the third part. The third part is to study the interaction effects of three parameters: sintering temperature, soaking time and combination addition between CaO and CaCO_3 on the two responses: fracture toughness and Vickers hardness of ZTA. The Design of Experiments (DOE) was implemented to reduce the number of tests and meanwhile the optimisation process was employed to optimise the effective range of responses. After applying Response Surface Methodology (RSM), it was proved that sintering temperature is the most influence parameter on the fracture toughness and hardness of ZTA ceramics. The optimum results (fracture toughness of $6.84 \text{ MPa.m}^{1/2}$ and hardness 1615 HV) obtained from sintering temperature at 1600°C , combination addition between CaO and CaCO_3 of 0.95 wt.%, and soaking time for 2.14 hr. The other designs such as Analysis of Variance (ANOVA), Lack of Fit (LOF), 3D mapping and Residual Analysis have also confirmed the adequacy of the result. However, confirmation results obtained from experiments found that the optimum results (fracture toughness $7.1 \text{ MPa.m}^{1/2}$ and Vickers hardness was 1584 HV) were obtained from 1.05 wt.% of combination addition between CaO and CaCO_3 into ZTA samples, sintering temperature of 1600°C and soaking time of 2.9 hr. These values are comparable with empirical formulas from RSM.

CHAPTER 1

INTRODUCTION

1.1. Research Background

Zirconia Toughened Alumina (ZTA) is an innovative and high performance ceramic compound which combines high strength, moderate toughness with high wear resistance and outstanding hardness (Kern *et al.*, 2015; Naga, Hassan and Awaad, 2015; Pfeifer *et al.*, 2016). Therefore, it is a promising candidate for structural materials such as motor, aerospace, cutting inserts, wear components, biomedical field, , implants, bushings, valve seats, dies, bearings, insulators, refractory uses, high temperature filtering, and armours (Maiti and Sil, 2011; Yao *et al.*, 2015; Xia *et al.*, 2016) It consists of the alumina (Al_2O_3) matrix which provides high strength and hardness and it is embedded with zirconia (ZrO_2) particles which promotes the fracture toughness. ZrO_2 is the intrinsic phase undergoes tetragonal to monoclinic phase transformation. This phase transformation is accompanied by approximately 4-6% volume expansion which causes stress induced transformation toughening and microcrack toughening. Consequently, compressive stress is produced around the crack tips which hampers crack propagation (Maiti and Sil, 2010; Sommer *et al.*, 2012).

ZrO_2 has three polymorphs: monoclinic (m), tetragonal (t) and cubic (c). The phase transformation of pure ZrO_2 is occurred with temperature variation. Hence, the fracture toughness of ZTA is based on this phase transformation (Jin, 2005). However, ZTA fracture toughness is still below the requirement for some engineering applications. Hence, many approaches have been taken to improve the fracture